

On the flexoviscous behavior in viscoelastic materials

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A phenomenological model on the relationship between viscoelasticity and flexoelectricity is proposed to address the electromechanical coupling under rheological processes in viscoelastic materials. Our theoretical studies show that some observed ferroelectric phenomena in certain viscoelastic materials, like polymer films, may not be intrinsic material behavior.

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There is currently a great deal of interest in electromechanical coupling phenomena in polymer films due to their potential technological applications. Although the piezoelectric effects (both the direct and the converse ones) and the corresponding pyroelectric effects in polymers had been observed before 1970s, the existence of the ferroelectricity in polymers was not recognized until the end of 1970s (Ref. [1] and references therein). However, there has been a concern about whether these phenomena are intrinsic material behavior or improper properties due to the inherent rheological or viscoelastic properties of polymers. Recent studies on the flexoelectricity in polymers have indirectly shown that the electromechanical coupling in viscoelastic materials may involve certain non-trivial collective and cooperative material behavior, which may not be explained by using conventional piezoelectric and flexoelectric models proposed for solid crystalline materials [2–4]. Those experimental observations stimulate us to consider the electromechanical coupling and the ferroelectric behavior in viscoelastic materials. To address our problems clearly, we start our discussion from a brief survey of piezoelectric and flexoelectric effects.

For non-centrosymmetric solid crystalline materials, their piezoelectric effects can be written as [5]

$$D_k = d_{ijk}^+ T_{ij} \quad (1)$$

and

$$S_{ij} = d_{ijk}^- E_k, \quad (2)$$

where D_k and E_k represent the induced electric displacement and the applied electric field, respectively; T_{ij} and S_{ij} represent the applied stress and the induced strain, respectively. Eq. (1) and Eq. (2) are usually called the direct piezoelectric effect and the converse piezoelectric effect, respectively; d_{ijk}^+ is defined as the piezoelectric coefficient for the direct piezoelectric effect and d_{ijk}^- the piezoelectric coefficient for the converse piezoelectric effect. For Hookean materials, we have $d_{ijk}^+ = d_{ijk}^-$ as required by equilibrium thermodynamics.

The inhomogeneous electromechanical energy coupling between the applied strain gradient and the induced electric polarization in solid crystalline materials, i.e., the direct type II flexoelectric effect, was proposed by Kogan in 1964 [6], which is given below.

$$D_m = \mu_{ijmk}^{II+} \nabla_k S_{ij}, \quad (3)$$

where ∇_k is the symbol representing the gradient with respect to the direction k ; μ_{ijmk}^{II+} is defined as the flexoelectric coefficient for the direct type II flexoelectric effect. For Hookean materials, we can easily write, via the Maxwell relations, the converse type II flexoelectric effect as [7, 8]:

$$T_{ij} = \mu_{ijmk}^{II-} \nabla_k E_m, \quad (4)$$

where μ_{ijmk}^{II-} is defined as the flexoelectric coefficient for the converse type II flexoelectric effect. Similarly, for Hookean materials, we have $\mu_{ijmk}^{II+} = \mu_{ijmk}^{II-}$.

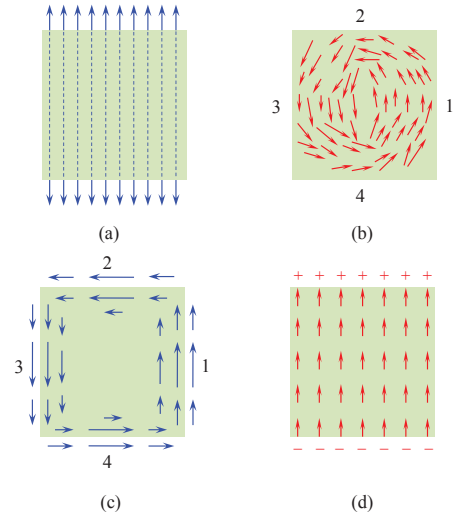


FIG. 1: (a) Uniform strain field; (b) gradient field of electric field; (c) gradient field of strain; (d) uniform electric field.

In 2007, Fu and Cross considered a situation where the Landau-Ginzburg-Devonshire (LGD) phenomenological model may not work properly in a gradient field of the

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order parameter in ferroelectric materials and proposed that there are two types of flexoelectric effects, the type I and the type II, existing in all solid crystalline dielectrics [8]. The phenomenological model of the type II flexoelectric effects is indeed the Kogan's phenomenological model given in Eqs. (3) and (4), whereas the type I flexoelectric effects are novel inhomogeneous electromechanical coupling phenomena predicted by Fu and Cross. The constitutive equations of this phenomenological model can be written as [8]:

$$\nabla_k D_m = \mu_{ijmk}^{I+} S_{ij} \quad (5)$$

and

$$\nabla_k T_{ij} = \mu_{ijmk}^{I-} E_m, \quad (6)$$

where μ_{ijmk}^{I+} and μ_{ijmk}^{I-} are defined as the flexoelectric coefficients for the direct and the converse type I flexoelectric effects, respectively. Clearly, $\mu_{ijmk}^{I+} = \mu_{ijmk}^{I-}$ for Hookean materials.

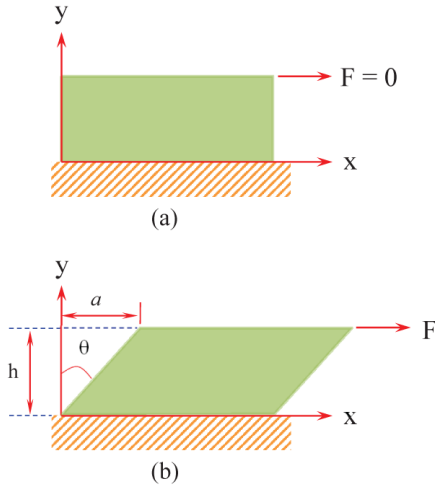


FIG. 2: A piece of material undergoing shearing driven by a force F ; (a) $F = 0$; (b) $F \neq 0$.

The physical pictures of the flexoelectric effects can be diagrammatically explained in a two-dimensional case shown in Fig. 1; mechanical energy and electrical energy are uniformly distributed in Figs. 1(a) and 1(d); electrical energy and mechanical energy are distributed in certain vortex patterns to form the electric displacement gradient shown in Fig. 1(b) and the stress gradient shown in Fig. 1(c). The energy coupling from Fig. 1(a) to Fig. 1(b) and from Fig. 1(d) to Fig. 1(c) represent the direct and the converse type I flexoelectric effects, respectively; the ones from Fig. 1(c) to Fig. 1(d) and from Fig. 1(b) to Fig. 1(a) represent the direct and the converse type II flexoelectric effects, respectively. In both cases shown in Figs. 1(b) and 1(c), the magnitude of the vertical electric displacement values and the vertical stress values reaches the maximum at spots 1 and 3

but these values are oriented in opposite directions, and reaches zero at spots 2 and 4; we can see the same situations at spots 2 and 4 and then at spots 1 and 3 in the horizontal values. From the viewpoint of equilibrium thermodynamics, these gradient fields are energetically more favorable since the vector values with opposite directions would cancel each other so that the resultant Gibbs free energy will decrease and approach a minimum value. Therefore, for a material undergoing such inhomogeneous electromechanical energy coupling, its molecules or atoms will be forced to move or rotate by a flexoelectric torque, which is generated during the coupling process by the inhomogeneously coupled energy, to form the aforementioned gradient fields. Unfortunately, compared with crystal binding energies, such a torque is too small to change crystalline structures of solid dielectrics so that the aforementioned vortex structures or gradient fields cannot be formed under normal conditions in solid dielectrics. However, for viscous materials like liquid crystals that can deform even under a very small stress, flexoelectric effects, especially the type I flexoelectric effects, could significantly change their molecular alignments and alter their properties [9]; for viscoelastic materials, flexoelectric effects may also have an influence on their properties. To make a reasonable and meaningful connection between flexoelectricity and viscosity in viscoelastic materials, we re-visit the concept of shear viscosity in purely viscous materials.

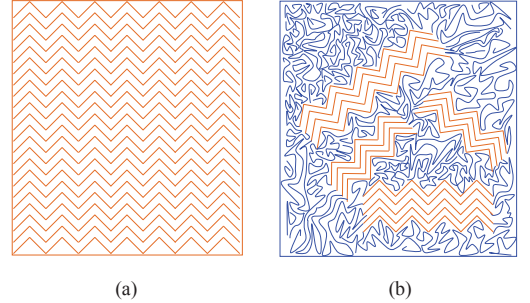


FIG. 3: (a) a perfect crystal (we use a zig-zag pattern to diagrammatically represent the crystalline structure); (b) a partially crystallized polymer with both the crystalline structure and the amorphous structure.

We consider a viscous material undergoing a rectilinear shearing flow, in which only the x-component of the rate of shear deformation is nonzero and is a linear function of y , driven by a force as diagrammatically shown in Fig. 2; its shear viscosity can be simply written as [10]:

$$\tau_x = \eta \partial u_x / \partial y, \quad (7)$$

where τ_x is the shear stress in the x-axis direction; u_x represents the rate of shear deformation in the x-axis direction; η is defined as the shear viscosity. For the viscous material, there is no relationship between the shear deformation and the driving force.

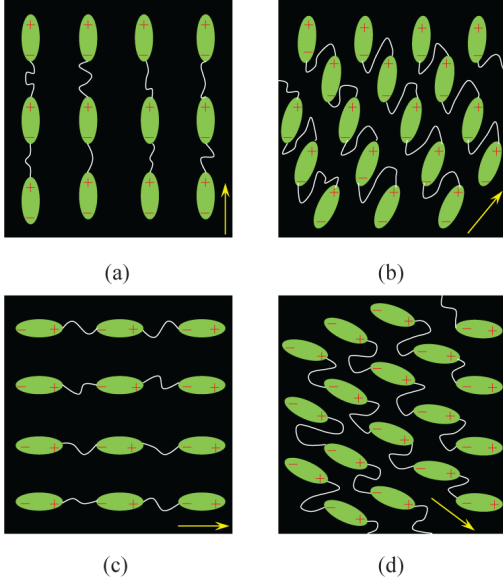


FIG. 4: Diagrammatic sketch of the formation of the tilted structures in polymers; (a) a polymer with a vertical molecular network; (b) the tilted structures induced by both flexoelectricity and flexoviscosity in the polymer given in (a); (c) a polymer with a horizontal molecular network; (d) the tilted structures induced by both flexoelectricity and flexoviscosity in the polymer given in (c).

For a Hookean material also diagrammatically shown in Fig. 2, Eq. (7) does not hold. The relationship between the shear deformation and the driving force can be defined as $\tau = G\theta$ ($\theta \ll 1$), here $\theta = a/h$ describes the shear deformation; $\tau = F/A$ (A is the top surface area of the material); and G is the shear modulus. Therefore, when F is removed, the shear deformation can be recovered completely.

For a viscoelastic material diagrammatically shown in

Fig. 2, when F is removed, the shear deformation can be recovered to a large extent shortly after the occurrence of the deformation; however, after longer times the recoverable deformation reduces. This is because the material possesses both viscous and elastic properties simultaneously. So we can re-write the Eq. (7) as:

$$\tau_x = \eta d(S_{xy})/dt, \quad (8)$$

where S_{xy} is the strain representing the gradient of the shear deformation in the y -axis direction. A universal shear viscosity relationship in viscoelastic materials is given below [11]

$$\tau_{ij} = \eta_{ijkl} d(S_{kl})/dt, \quad (9)$$

where η_{ijkl} represents the usual viscosity tensor.

Substituting the strain tensor term in Eq. (2) into Eq. (9), we obtain the following relationship between piezoelectricity and viscosity in non-centrosymmetric viscoelastic materials,

$$\tau_{ij} = \eta_{ijkl} d_{klm}^- d(E_m)/dt = \gamma_{ijm} d(E_m)/dt, \quad (10)$$

where γ_{ijm} is defined as the piezoviscous coefficient. This equation demonstrates a linear relationship between the applied time-varying electric field and the induced shear stress. The phenomenon is defined as the piezoviscous effect or *piezoviscosity*.

By taking the partial derivative of both sides of Eq. (9) with respect to m , we obtain a modified equation shown below,

$$\nabla_m \tau_{ij} = \eta_{ijkl} d(\nabla_m S_{kl})/dt. \quad (11)$$

Substituting the strain gradient term embodied in Eq. (6) into Eq. (11), we have the following relationship between the type I flexoelectricity and viscosity in viscoelastic materials,

$$\nabla_k \tau_{ij} = \eta_{ijuv} s_{ijuv} \mu_{ijmk}^{I-} d(E_m)/dt = \rho_{ijmk}^I d(E_m)/dt, \quad (12)$$

where ρ_{ijmk}^I is defined as the type I flexoviscous coefficient; s_{ijuv} represents the compliance tensor. The equation describes a linear relationship between the applied time-varying electric field and the induced inhomogeneous shear stress. For simplicity, we define this phe-

nomenon as the type I flexoviscous effect.

Similarly, by substituting the strain tensor term embodied in Eq. (4) into Eq. (9), we have the following relationship between the type II flexoelectricity and viscosity in viscoelastic materials,

$$\tau_{ij} = \eta_{ijuv} s_{ijuv} \mu_{ijmk}^{II-} d(\nabla_k E_m)/dt = \rho_{ijmk}^{II} d(\nabla_k E_m)/dt, \quad (13)$$

where ρ_{ijmk}^{II} is defined as the type II flexoviscous coef-

ficient. Eq. (13) demonstrates a linear relationship be-

tween the applied time-varying inhomogeneous electric field and the induced shear stress. The phenomenon is defined as the type II flexoviscous effect. Both type I and II flexoviscous effects, for simplicity, can be called *flexoviscosity*.

It is interesting to note that d_{klm}^- appears in Eq. (10), and μ_{ijmk}^{I-} and μ_{ijmk}^{II-} appear in Eq. (12) and Eq. (13), respectively; but d_{klm}^+ , μ_{ijmk}^{I+} , and μ_{ijmk}^{II+} cannot be found in those equations. Of course, d_{klm}^+ , μ_{ijmk}^{I+} , and μ_{ijmk}^{II+} should have certain relationships with the viscosity tensor, but these relationship would be different from Eq. (10), Eq. (12), and Eq. (13), which means that $d_{klm}^- \neq d_{klm}^+$, $\mu_{ijmk}^{I-} \neq \mu_{ijmk}^{I+}$, and $\mu_{ijmk}^{II-} \neq \mu_{ijmk}^{II+}$ in viscoelastic materials.

Perhaps, it is more interesting to use the concepts of flexoelectricity and flexoviscosity to analyze dielectric and mechanical behavior of polymer materials since they are not only viscoelastic materials but also possess the following two characteristics: (a) electric charges can be easily trapped and stored in polymers, especially some highly insulating polymers, for extremely long periods of time; therefore, they are often regarded as quasi-electret materials [12]. Thus for polymer materials, E_m given in Eq. (4), Eq. (6), Eq. (10), Eq. (12), and Eq. (13) should be substituted by $E_m^{ext} + E_m^{tc}$, here E_m^{ext} is the applied electric field and E_m^{tc} is the electric field generated by the trapped charges. This means that, even without E_m^{ext} , the fluctuation of E_m^{tc} due to the thermally excited hopping of electrons from one isolated state to another in polymers could gradually alter their long chain molecular structures via flexoelectricity (the short-term effect) and flexoviscosity (the long-term effect); (b) the molecular structures of polymers are usually very complicated. A perfect crystal and a semicrystalline polymer are diagrammatically compared in Fig. 3. Being different from a perfect crystal, a semicrystalline polymer has inherent heterogeneous structures like a “*spontaneous composite*” formed with crystalline parts in a glassy matrix [13]. The mutual interactions between crystalline phases and amorphous phases and among different amorphous phases in polymers could dominate their material properties. For example, piezoelectric responses have been detected in non-piezoelectric polymer films [3, 4]. Therefore, the electromechanical coupling in polymers should be certain collective and cooperative material behavior, which is different from that in solid piezoelectric materials.

From Fig. 3(b), we can see that neither electrical energy nor mechanical energy can be uniformly distributed in polymer materials. So it is convenient to use the converse type I flexoelectric effect defined by Eq. (6) and the type I flexoviscous effect defined in Eq. (12) to analyze the formation of flexoelectric domains or gradient field related structures in polymers. Here, we only give a qualitative analysis on the formation of these structures. We assume that there is a single polymer layer with a simple vertical molecular network shown in Fig. 4(a); the

network would be altered via flexoelectricity and flexoviscosity to form a tilted molecular structure shown in Fig. 4(b); similarly, we can see another layer with a horizontal molecular network shown in Fig. 4(c) and the corresponding layer with a tilted molecular structure shown in Fig. 4(d). Imagining that a polymer film consists of many single layers shown in Fig. 4, we can see that some tilted and layered structures would be formed and preserved (due to viscoelasticity) in the film; the ensemble of these structures looks like a helix-like structure in three-dimensional space. Before discussing the influence of these structures on material properties of the film, we revisit Meyer’s pioneer work on ferroelectric liquid crystals. In 1970s, Meyer proposed that the liquid crystal with the chiral smectic C phase or the smectic C* phase should be ferroelectric [14]. Meyer’s creative argument is based on the point group symmetry analysis; he argued that chiral molecules lack the inversion symmetry and their tilted and layered phases would be non-centrosymmetric, which renders the existence of ferroelectricity in the liquid crystal. In polymers, molecules might not be chiral and the aforementioned tilted and layered structures might not be non-centrosymmetric; however, those tilted and layered structures could create a non-uniform spatial distribution of the induced charges (induced by, for example, the electromechanical coupling) and the trapped charges and generate “*a quasi-permanent electrical potential oriented along a specific direction*” (which is different from the electrical potentials randomly induced by the trapped charges) in polymers, which could exhibit a “*spontaneous electric polarization*” that can be reversed by the application of an external electric field. The reason that such an electrical potential can be preserved over relatively long periods of time and does not dissipate is due to the viscoelastic behavior in polymers. Therefore, we can argue that some observed P-E hysteresis loops in polymer films might be improper ferroelectricity. Experimental studies are now underway to verify the arguments addressed here.

Last but not least, the process of the formation of the tilted and layered structures diagrammatically demonstrated by Fig. 4 should be accompanied by material property variations, especially mechanical and dielectric properties, in polymer films, which can be seen clearly in Fig. 4. This means that the phenomenological model, flexoelectricity and flexoviscosity, could provide us with a broader perspective for understanding the physical aging phenomena of polymers.

In summary, we propose here a phenomenological model on the relationship between viscoelasticity and the electromechanical coupling in viscoelastic materials, i.e., the flexoviscous effect and the piezoviscous effect. According to the model, the thermodynamic equivalence between the direct and the converse flexoelectric and piezoelectric effects is broken in viscoelastic materials. The extended physical picture of the model is that the long chain molecular structures of polymers could be altered via flexoelectricity and flexoviscosity to form

certain tilted and layered structures, which could induce ferroelectricity-like behavior in polymers. Therefore, some observed ferroelectric phenomena in polymer films might be improper properties.

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